

Utilization of industrial granitic waste as adsorbent for phosphate ions from wastewater

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Abstract

Recently, Granite waste is represented as one of the natural wealth which could be exploited by eco-friendly methods. In the current research, innovative application of using raw and fired granitic waste powder in the field of water treatment depended on the adsorption process by its two main mechanisms (chemical and mycological). The aimed metal that the granitic wastes play an important role on its removal is phosphate ion from wastewater. Achievement of the aim of the recent research was required firstly, studying most of physical, chemical and mineralogical characterization of studied granitic waste using different laboratory techniques such as XRD, XRF, Scanning electron microscope (SEM), FTIR and leaser particle size. Secondly different affecting chemical parameters including pH, contact time, adsorbent dose, metal concentration at ambient temperature were studied and statically represented by Langmuir and Freundlich isotherm for granitic waste powder and immobilized waste with *Aspergillus niger*. The integration of the promising obtained results leads to the allowance of using such granitic waste powder in removal of phosphate ions from wastewater.

Keywords— Granitic wastes, phosphate ions, wastewater treatment, *Aspergillus niger*, eco-friendly waste, mycological, fired granite.

1. INTRODUCTION

Granite as ornamental stone should be defined as visibly granular, igneous rock ranging in color from pink to light or dark gray consisting mostly of quartz and feldspars accompanied by one or more mafic minerals [1]. Accumulation of ornamental stone waste such as granite would increase the environmental problems in surrounding area so, most countries of the world are paying attention and clear the need to recycle such these waste [2]. Generally, it can be reported that two main types of granitic waste, the first one named granitic quarry waste whereas, the second type called granitic industrial powder which is generated by the stone crushing industry accumulated from sawing over years. The recent research deals with the second form (i.e. Granitic industrial powder).

Several studies had been carried out to organize such granite waste in different engineering applications for instance "[3],[4]". In the current work, innovative application of using granite waste powder in water treatment by adsorption method.

Physically, Adsorption is a surface process that leads to transfer of a molecule from a fluid bulk to solid surface. This can occur because of physical forces or by chemical bonds. Usually it is reversible (the reverse process is called desorption); then it is responsible not only for a subtraction of substances but also for release [5].

Although, the importance Phosphorous as phosphate ions is one of the important soil elements for living organisms but the excess of phosphate concentration in the effluent discharge can lead to eutrophication of the receiving confined wastewaters [6]. Consequently, the amount of phosphate in domestic and industrial discharges must be controlled using

wastewater treatment technology [7]. Therefore, various methods including chemical, physical and biological have been established for phosphate removal in the industrial and domestic effluent in order to avoid eutrophication.

Phosphate ions removal from water can be achieved by several methods including biological removal [8], [9], ion exchange [10], and electrocoagulation [11]. Chemical method is widely accepted, such as lime, alum and ferric chloride are the common precipitants used for phosphate removal [12] but its cost and sludge productions make chemical treatment an unattractive option for wastewater treatment [13].

Nowadays, several studies have been focused on the use of low cost adsorbents. Cost effectiveness is the prime criterion in the selection of a sorption technology whether it uses natural or synthetic sorbents [14]. Phosphate can be removed from water using sorbents such as natural geological raw materials (calcite, oxides of iron and goethite (FeOOH), active red mud, and activated carbon). One of the problems encountered with these sorbents is that they have very low sorption capacities [15]. Moreover, some previous studies have been conducted with using of different stone processing waste particularly marble by-products as adsorbents for both of lead and phosphate removal from waste water "[16], [17]".

On the other hand, the second method that can be used for removal of phosphate ions from wastewater called biosorption method which can be expressed by means of adsorption and biodegradation mechanism were involved in the removal process. Generally, the previous process can be occurred when fungal biomass removes considerable amounts of organic pollutants from aqueous solution through adsorption [18]. A detailed review of heavy metal biosorption by fungi can be found elsewhere [19]. Biosorption of organic pollutants by

various types of fungal species [20]. *Aspergillus terreus* and *Aspergillus niger* showed excellent pollutant removal capabilities. Whereas, *Aspergillus terreus* showed the best result for removal of nitrate and BOD while *Aspergillus niger* showed best removal of phosphate and COD from wastewater [21]. The recent research, focused on adsorption process of phosphate ions from wastewater by raw and fired granitic waste powder. The aim of the recent research also involved the role of microorganism (*Aspergillus niger*) in increasing the phosphate removal efficiency from wastewater.

2. MATERIALS AND METHODS

2.1. Materials:

The achievement of the aim of the recent research the usage of the following studied materials have been required as following. First one is the granitic waste both of raw granitic waste and its derivative fired granitic waste as shown in fig 1. The source of the studied granitic waste is air-dried powder residual from the stone cutting landfill at ShaqEl-Thoban area, east of AutoStrad road, Cairo Governate as in fig 2.



Fig. 1. Raw granitic powder and fired granitic powder.



Fig. 2. The source of the studied granitic waste

The second studied type of granitic waste called fired granitic waste that derived from granitic waste by firing it at 1000°C. The effect of the two previous types have been studied and compared as adsorbent material for phosphate ions from used wastewater. The wastewater has been collected from the pretreatment stage of Abu Rawash plant in clean and steri-

lized bottles. Moreover, some chemicals and reagents were involved in the recent research including: Sodium hydroxide (NaOH, 99% pure, Oxford Co.), Hydrochloric acid (HCl, 95-97%, Honey well Co.) Mono potassium phosphate (KH₂PO₄, 99%, Honey well Co.).

To complete the aim of this study *Aspergillus Niger* was isolated from Abu Rawash wastewater treatment plant and used for biosorption of phosphate ions from used wastewater. As it was the most dominant fungal strain according to" [22, 23]"

2.2. METHODS AND TECHNIQUES:

2.2.1. Raw and fired granitic waste characterization

Some laboratories techniques have been carried out within the current research to evaluate the ability of studied raw and fired granitic waste as adsorbent material for phosphate ions from wastewater. Some of these techniques focused on the different characterization of the raw and fired granitic wastes include: (X-ray diffraction (XRD), X-ray Fluorescence (XRF), Scanning electron microscopy (SEM), Particle Size Distribution (PSD) and Fourier transform infra-red spectroscopy (FT-IR).

As (XRD model X \square Pert ProPhillips MPD PW 3050/60 X-ray diffractometer used for detailed mineralogical composition of raw and fired granitic wastes while XRF (Phillips PW 1400 Spectrometer), Holland used to determine the major oxides of raw and fired granitic wastes before and after adsorption process. On the other hand, scanning electron microscopy (SEM) was used to determine microstructure and morphological features of both raw and fired granitic wastes by using SEM model Quanta 250 FEG (field emission gun) attached with accelerating voltage 30 K.V. FEI company (Netherlands). Raw and fired granitic wastes were identified using a Jasco-6100 Fourier transformed infrared spectrometer (FTIR; Varian model, Excalibur FTS 3000MX, Paolo Alto, CA, USA).

The tested samples were prepared using the KBr pressed disc technique. The analysis was done between 400- 4000 cm⁻¹. The particle size distribution of the used raw and fired granitic wastes was determined using a laser diffraction analyzer (manufactured by Horiba LA-950, France).

2.3. Batch Experimental System

Adsorption experiments were conducted by stirring the 50 ml of potassium phosphate solution with concentration 30 mg/L with 1 g used granitic waste in the capped conical flasks at 25+ 2° C for 120 min. and shacked at 150 rpm. The adsorption of potassium phosphate solution was studied using granitic waste by batch technique. After equilibration, the suspension of the adsorbent was separated from the solution by filtration using filter paper Whatman No. 2 and the concentration of phosphate remaining in solution was measured using UV visible Spectrophotometer (ICE 3300, Thermo Scientific Ltd., UK). The percentage of removal efficiency was calculated using

Equation 1. The amount of phosphate sorbed by weight of granitic waste was calculated using equation 2.

$$\text{Sorption (\%)} = (C_0 - C_e) / C_0 * 100 \quad (1)$$

Where C_0 is the initial concentration of phosphate ions in solution, mg/l.

C_e is the equilibrium concentration of phosphate ions in solution, mg/l.

$$Q_e \text{ (mg/l)} = (C_0 - C_e) * V/m \quad (2)$$

Where Q_e is the equilibrium adsorption capacity, mg/g.

V is the volume of aqueous solution, L.

m is the dry weight of adsorbent, g.

2.3 Effect of operating parameters

2.3.1 Effect of pH

About 1 g of raw granitic waste/fired granitic waste was added to 30 mg/L of phosphate solution at different pH values (3-11) at temperature $25 \pm 2^\circ\text{C}$ and the stirring of the solution was fixed at 150 rpm. The pH was adjusted using NaOH to provide an alkaline medium and HCL to provide acidic medium.

2.3.2 Effect of contact time

About 1 g of raw granitic waste/fired granitic waste dosage was added to 30 mg/L of phosphate solution at different contact times namely (30-180 minutes), temperature $25 \pm 2^\circ\text{C}$, at pH 9 ± 0.2 and the stirring of the solution was fixed at 150 rpm.

2.3.3 Effect of adsorbent dose

Different adsorbent dose (0.5-3 gm) of raw granitic waste/fired granitic waste dosage was added to 30 mg/L of phosphate solution for 150 minute at temperature $25 \pm 2^\circ\text{C}$ and pH 9 ± 0.2 .

2.3.4 Effect of initial phosphate concentration

At room temperature, 1 g/L dosage of raw granitic waste/fired granitic waste, was added in solutions with different initial phosphate concentration (5.0, 10.0, 15, 20.0, 25.0, and 30.0 mg/L) at temperature $25 \pm 2^\circ\text{C}$ and pH 9 ± 0.2 .

2.4. Sampling and isolation

The wastewater samples were collected in sterile bottles from Aborawash wastewater treatment plant and then placed in icebox to prevent decomposition during transport to the laboratory. Serial dilution and plate count technique were employed [24]. Three replicates aliquots of one milliliter of diluted sample (1:1) were plated onto Sabouraud's Dextrose Agar (SDA) solid medium to ensure the growth of *Aspergillus niger* present in the samples. *Aspergillus niger* identification tests were performed in the Regional Center for Mycology and Biotechnology (RCMB), Al-Azhar University, Cairo, Egypt, by

subjecting the fungal isolates to a certain morphological studies by an image analysis system using Soft- Imaging GmbH software (analysis Pro ver. 3.0) [25], [26]. The duration of incubation is three to seven days of at 28°C , developed up colonies were isolated. The purified isolates were obtained by streaking colonies repeatedly on SDA medium then observed and identified microscopically based on standard manuals [27],[28].

2.5. Biomass production

A.niger strain has been cultivated on Sabouraud's Dextrose Broth Medium (SDB) liquid medium for 7 days of incubation at 28°C , the filtrated biomass was washed with doubled-distilled water dried at room temperature and used for the biosorption studies as shown in fig 3.

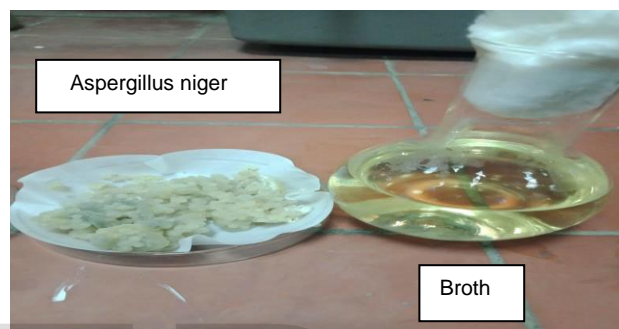


Fig. 3. Biomass production of *Aspergillus niger*.

2.6. Biosorption studies

The biosorption experiments were performed by the interaction of the *Aspergillus niger* biomass with 50 mL of potassium phosphate solution with concentration 30 mg/L with 1 g of granitic waste with dried biomass in the capped conical flasks at 25°C for 120 min.

3. RESULTS AND DISCUSSION

3.1. Result

3.1.1. Granitic waste characterization:

Mineralogically, XRD has been conducted for representative samples of both raw granitic waste and also fired one as shown in XRD diffractogram fig 4. It can be detected the following by XRD:

Firstly, the studied granitic waste most likely to be originated from Alkali-Feldspar granite. Secondly, similarity in mineralogical composition between both studied samples of raw and fired granitic waste as both consist essentially of quartz, albite and microcline with minor biotite which disappeared in fired granitic waste as shown in fig 4.

The disappearance of biotite mineral from fired granitic waste most likely to be due to its small amount and relatively low intensity of dehydroxylation effect approximately at 1000°C [29].

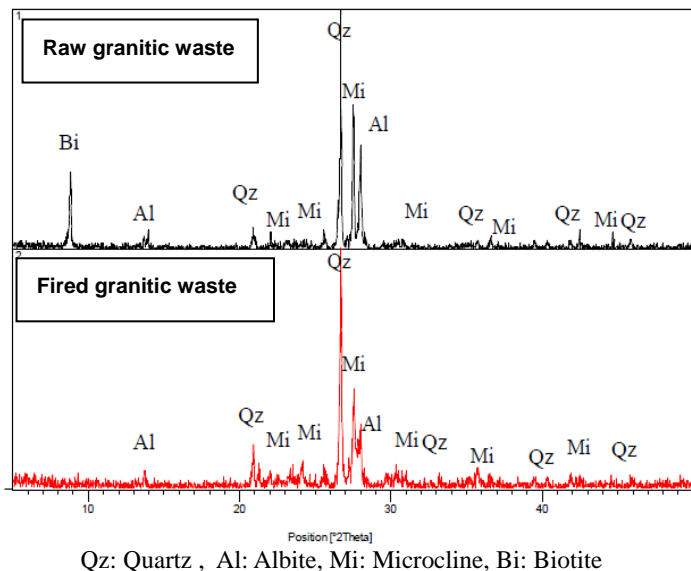


Fig. 4. XRD diffractograms of the studied raw and fired granitic waste.

Chemically, in the recent study 4 studied samples have been analyzed by XRF two of these samples are representative for granite industrial waste and it's fired one before treatment while others are granite waste and it's fired one but after treatment (adsorption) process. All of the previous studied samples have been listed in table (1).

The obtained results revealed that, the chemical composition of the studied samples is relatively similar as SiO_2 % is the main major oxides by percentage followed by Al_2O_3 which represents the second major oxide for all studied samples. Moreover, it appears relatively enrichment in alkalis ($\text{K}_2\text{O} + \text{Na}_2\text{O}$ %) as the used granite powder waste is belong mineralogically to Alkali-feldspars granite. It can be also observed that Fe_2O_3 , CaO and MgO % nearly with the same percentage in all of the studied samples. All other oxides present as traces.

Regardless that P_2O_5 % is also present as traces but the relative enrichment of its percentage content in treated samples than raw studied samples it can be used as pathfinder for the role of granite industrial waste as adsorbent for removal phosphate ions process as shown in fig 5.

On the other hand, the chemical changes in studied samples can be detected through treatment adsorption process by following the percentage of used waste forming oxides as SiO_2 , Al_2O_3 , Na_2O and MgO % have been decreased in both raw and fired granite industrial waste as illustrated in fig 5. It can be also reported the opposite case for K_2O , Fe_2O_3 , CaO and P_2O_5 % which have been increased after adsorption as shown in table (1).

TABLE 1
Chemical composition and LOI of the materials used.

	Raw granitic waste	Fired granitic waste	Raw granitic waste after treatment	Fired granitic waste after treatment
SiO_2	67.40	67.96	66.1	66.3
Al_2O_3	14.00	14.00	13.70	14.20
K_2O	5.15	5.56	6.43	6.72
Fe_2O_3	4.12	4.08	4.37	4.23
Na_2O	2.95	2.74	2.49	2.62
CaO	2.48	2.70	3.01	3.14
MgO	0.94	0.87	0.79	0.70
TiO_2	0.58	0.57	0.59	0.65
P_2O_5	0.17	0.20	0.23	0.21
Cr_2O_3	0.17	0.06	0.05	0.08
BaO	0.15	0.14	0.13	0.15
SO_3	0.13	0.08	0.18	0.19
MnO	0.06	0.06	0.09	0.06
ZrO		0.05	0.04	0.05
Cl	0.05	0.04	0.05	0.1
L.O.I	1.57	0.45	1.57	0.45
Total	99.9	99.98	99.81	99.84

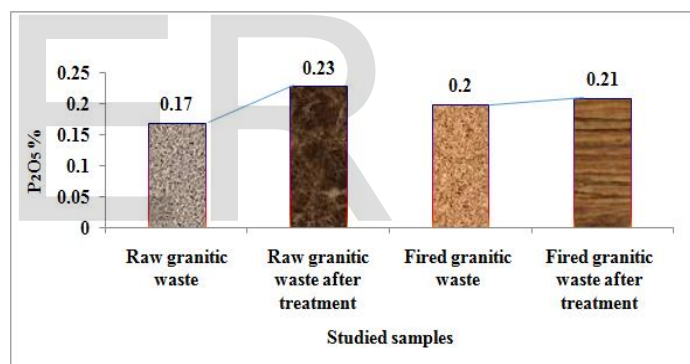


Fig. 5. The change in the percentage of P_2O_5 % through all of the studied granitic waste sample before and after adsorption process.

The particle size distribution of raw and fired granitic waste illustrated in bimodal peaks fig 6a, 6b respectively. Moreover, it can be noticed that for raw granitic waste the biggest quantitative percentage that are found at 4.3% and 2.9% with mean size 27.7 μm . On the other hand the fired granitic waste showed its biggest quantitative percentage at 4.5% and 4% with mean size 30.7 μm . Generally, both of raw granitic waste and fired one are within coarse silt size.

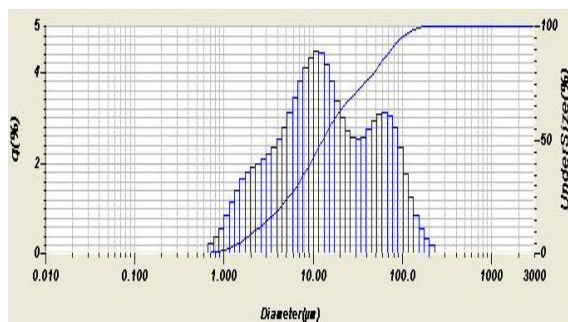


Fig. 6a. Leaser particle size distribution pattern of the used raw granitic waste.

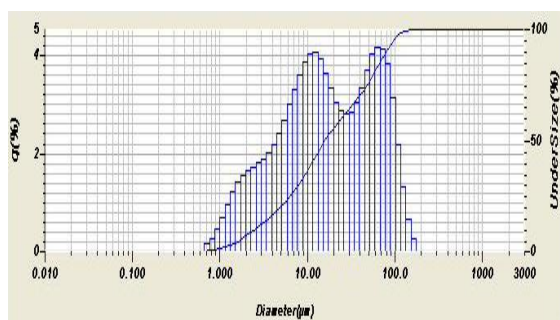


Fig. 6b. Leaser particle size distribution pattern of the used fired granitic waste.

As shown in fig 7 SEM revealed that the main morphological features approximately the same for both studied raw and fired granitic waste as it has the same main crystal shape and nearly the same size. The main difference is the increase in porosity and pore- space between crystals of fired granitic waste due to subject to firing process at 1000 ° C.

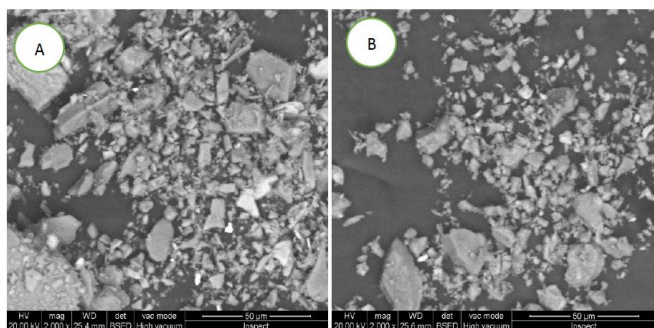


Fig. 7. SEM micrographs of the different studied granitic waste powder.
A) Raw granitic waste powder, B) Fired granitic waste powder

3.1.2 Results of Fourier transformed infrared spectrometer (FTIR) analysis of raw and fired granitic waste powder.

FTIR spectra of raw and fired granitic waste powder are represented in fig 8 the matching in the band locations is obvious in the two spectra. There are different transmittance bands related to symmetric stretching vibration of Si-O-Si (Al) (at 1010-

1018 Cm^{-1}), asymmetric stretching vibration of Si-O-Al (at 685 - 774 Cm^{-1}), stretching vibration of S-O (within sulphate group at 1147 Cm^{-1}). There is a stretching vibration of H OH at 1627-1630 Cm^{-1} and bending vibration of OH group at (3428-3431 Cm^{-1}). There are no differences between the spectra of raw and fired granitic waste powder. Nevertheless, a shift into lower wavenumber was identified.

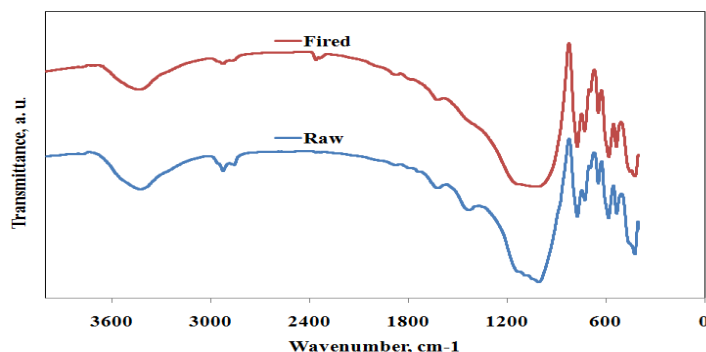
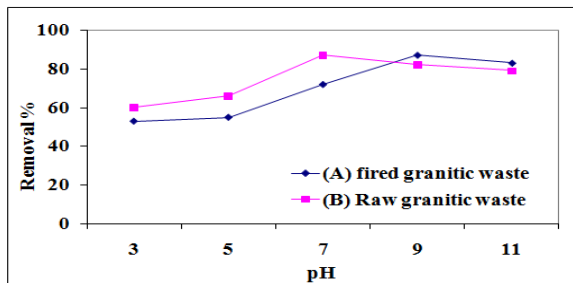


Fig. 8. FTIR spectra of raw and fired granitic waste Powder.

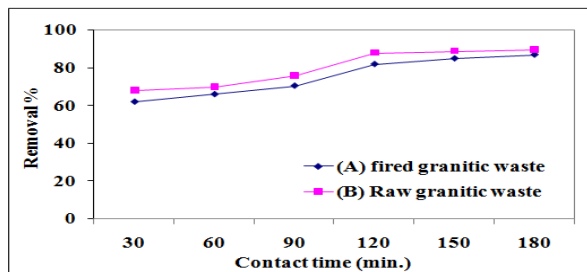
Based on the different studied criteria for raw and fired granitic waste within the current study, it can be revealed that both of fired and raw granitic wastes have been showed approximately symmetrical in mineralogical, chemical and morphological criteria. Moreover, the main difference between raw and fired studied granitic waste is the relative increase in pore space between studied fired granitic waste as the detected by SEM most likely to be according to the disappear of biotite mineral in the case of fired granitic waste as previously shown by XRD pattern.

3.1.3. Chemical factors affecting the removal of phosphate ions.

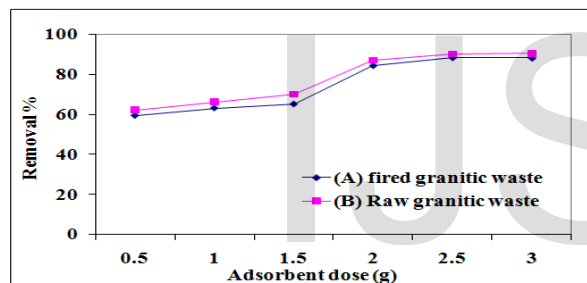
Four main parameters affecting the adsorption process ions from wastewater by both studied raw and fired granitic waste. It includes the following pH, contact time, adsorbent dose and initial metal concentration. All of the previous studied parameters have been conducted for raw and fired granitic waste with diagrammatically plotting as shown in fig 9. Firstly, based on fig 9A it can be revealed that the phosphate removal shows maximum at pH 9 solution and then decreases with further increase in pH from 10 to 11. Significant enhancement of adsorption was achieved at about pH 9 Fig 9A. Secondly, the contact time in adsorption of phosphate ions is attained at about 150 minutes of stirring time throughout the study as in fig 9B. Thirdly, its observed that the maximum adsorption obtained at 2.5 gm under the conditions of pH 9 and contact time 150 minutes fig 9C. Fourthly, the phosphate removal efficiency increases with increasing phosphate concentrations and rises to maximum up to around 25 to 30 mg/l as shown in fig 9D. Generally throughout the previously mentioned affecting parameters both of raw and fired granitic wastes have been exhibited approximately the same agreed with [7].



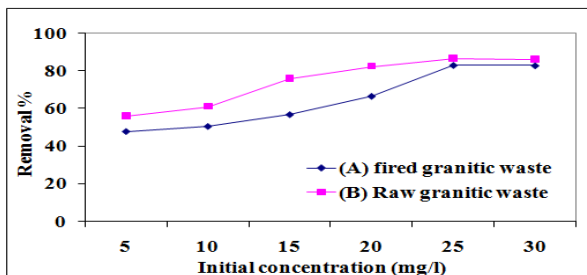
(A)



(B)



(C)



(D)

Fig. 9. Effect of variation in pH, contact time, adsorbent dose and initial metal concentration on adsorption of phosphate ions on raw granitic waste/fired granitic waste.

The following table (2) exhibits phosphate removal % in correspondence with obtained optimum chemical parameters affecting the adsorption of phosphate ions by studied raw and fired granitic wastes at ambient temperature 25°C. therefore it can be observed that there is no detectable difference between the phosphate removal % by both raw and fired granitic wastes.

TABLE 2

Optimum chemical parameters for phosphate removal % by raw and fired granitic waste.

Optimum chemical parameters	Phosphate removal % Raw granitic waste	Phosphate removal % Fired granitic waste
pH (9)	82	87
Contact time (150 min)	86.5	83.2
Adsorbent dose (2.5gm)	90.2	88.2
Phosphate concentration (25-30 mg/l)	89	85

3.1.4. Adsorption models

3.1.4.1 Adsorption isotherm

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase since the adsorption isotherms are important to describe how adsorbates will interact with the adsorbents so there are critical for design purposes; therefore, the correlation for equilibrium data using an equation is essential for practical adsorption operation [30].

Two isotherm equations were adopted in this study as follows:

3.1.4.2 Langmuir isotherm equation

The Langmuir equation is based on the assumptions that maximum adsorption corresponds to a saturated mono-layer of adsorbent molecules on the adsorbent surface, that the energy of adsorption is constant [31]

The Langmuir equation is defined as:

$$Q_e = (b \cdot Q_m \cdot C_e) / (1 + b \cdot C_e) \quad (1)$$

And in linearized form is:

$$C_e / Q_e = (C_e / Q_m) + (1 / (b \cdot Q_m)) \quad (2)$$

Where “Q_m” and “b” are Langmuir constants related to the adsorption capacity and sorption energy, respectively. “C_e” is the equilibrium concentration in mg/l, and “Q_e” is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). The plots C_e / Q_e against C_e are shown in Figure (10). The adsorption of phosphate ions on raw granitic waste/fired granitic waste gives a straight line. It is clear that the linear fit is fairly good and enables the applicability of Langmuir model. The calculated Langmuir constants were listed in table (3).

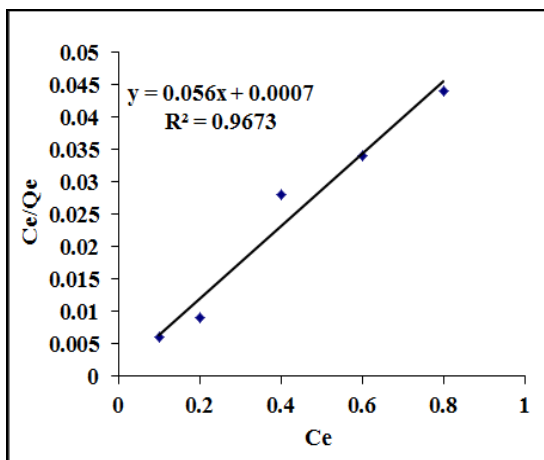


Fig. 10a. Langmuir isotherm plot for adsorption of phosphate ions on raw granitic waste.

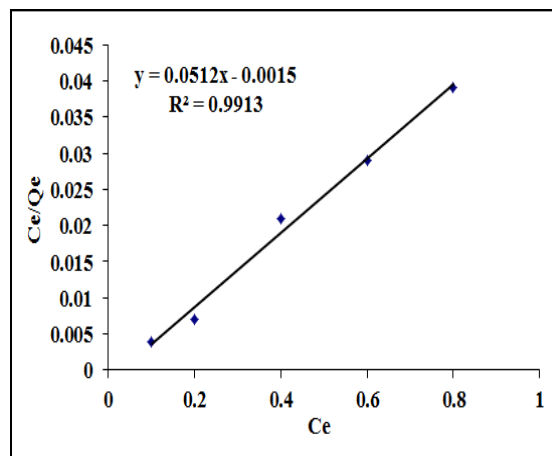


Fig. 10d. Langmuir isotherm plot for adsorption of phosphate ions on fired granitic waste immobilized with *Aspergillus niger*.

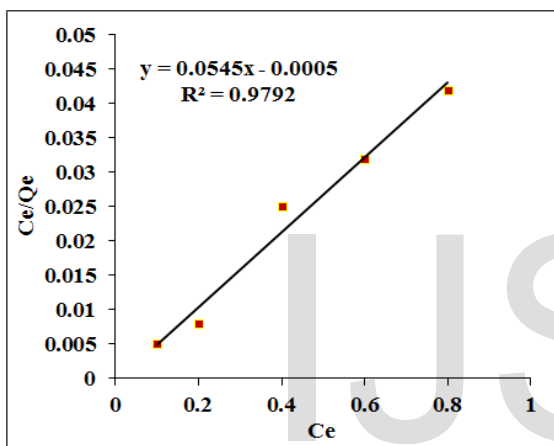


Fig. 10b. Langmuir isotherm plot for adsorption of phosphate ions on fired granitic waste.

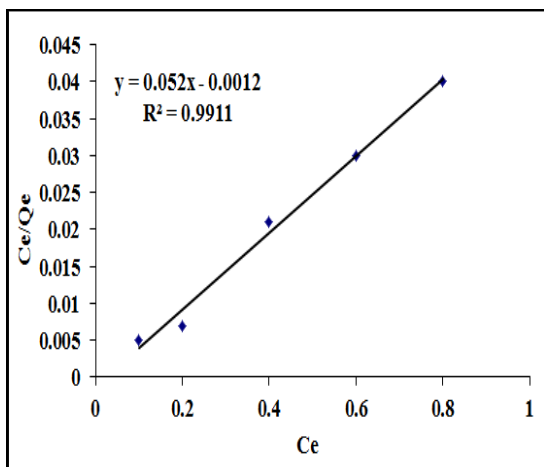


Fig. 10c. Langmuir isotherm plot for adsorption of phosphate ions on raw granitic waste immobilized with *Aspergillus niger*.

TABLE 3

Langmuir constants calculated from Langmuir isotherm.

	R2	qm	b
Raw granitic waste	0.967	14.92	220.9
Fired granitic waste	0.979	16.42	250.5
Raw granitic waste immobilized with <i>Aspergillus niger</i>	0.991	12.92	200.9
Fired granitic waste immobilized with <i>Aspergillus niger</i>	0.9913	13.42	220.5

As observed, experimental data were fitted to Langmuir equation, and therefore it is suitable for the analysis of kinetics. The correlation coefficient R2 for the Langmuir isotherm is achieved the requirement of the equation. As shown in table (3) R2 moves within narrow range (0.967-0.979) in raw granitic waste and fired granitic waste. It can be also, revealed that the presence of relative increase in the case of addition of *Aspergillus niger* to the granitic wastes (0.991-0.9913) which indicates that relative increase in the adsorption efficiency of phosphate ions from wastewater.

3.1.4.3 Freundlich isotherm equation

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.

$$Q_e = k. C_e^{1/n} \quad (3)$$

and in linearized form is :

$$\text{Log } Q_e = \log k + (1/n) \log C_e \quad (4)$$

Where "C_e" is the equilibrium concentration of the adsorbate (mg/l), "Q_e" amount of adsorbate adsorbed per unit weight of adsorbent (mg/g), "k" is a frendlish constant a parameter related to the temperature and "n" is a characteristic constant for the adsorption system under study. The plots of log Q_e against log C_e are shown in fig 11, the adsorption of phosphate ions onto raw granitic waste/fired granitic waste give a straight line; values of "n" between 0.5 and 10 show good adsorption [32]. The calculated Freundlich constants were listed in table (3).

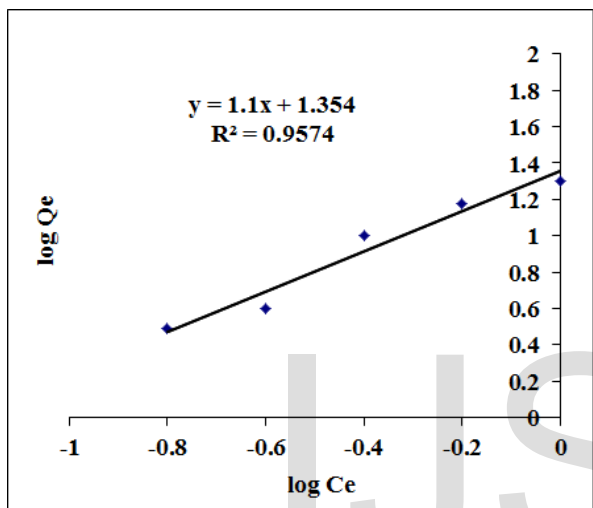


Fig. 11a. Freundlich isotherm plot for adsorption of phosphate ions on raw granitic waste.

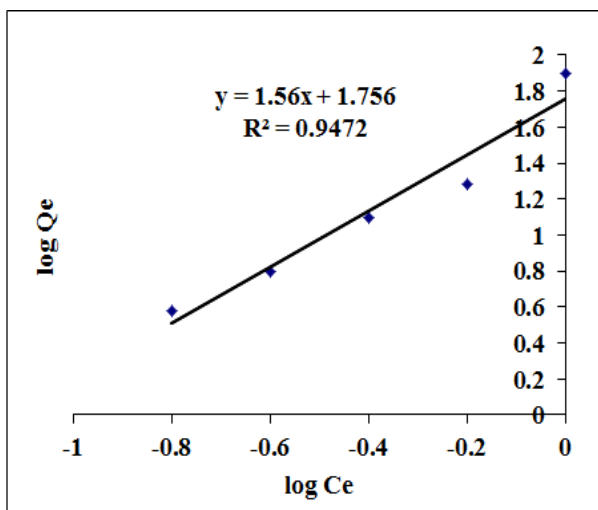


Fig. 11b. Freundlich isotherm plot for adsorption of phosphate ions on fired granitic waste

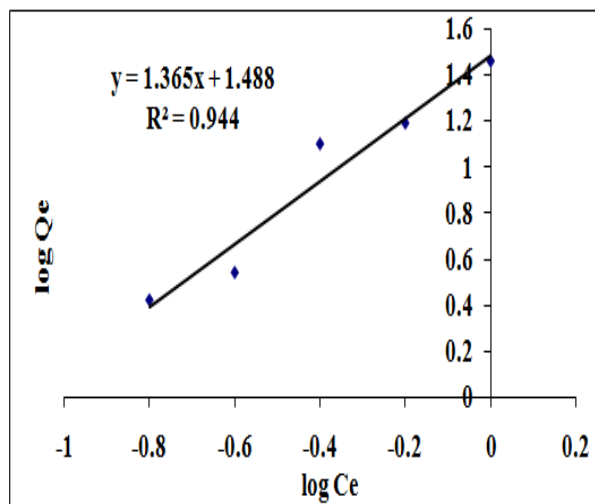


Fig. 11c. Freundlich isotherm plot for adsorption of phosphate ions on raw granitic waste immobilized with *Aspergillus niger*

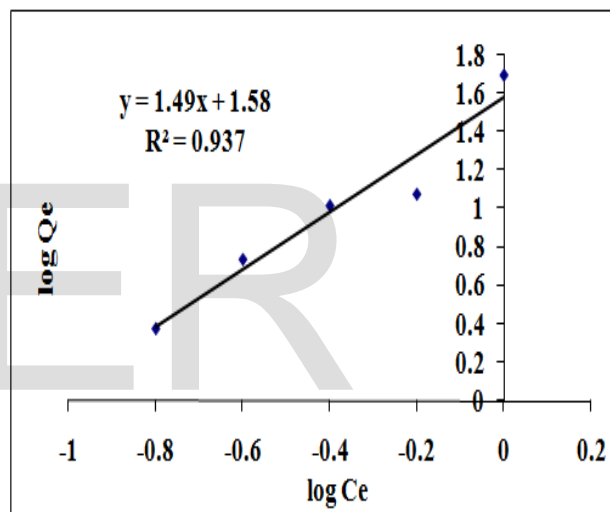


Fig. 11d. Freundlich isotherm plot for adsorption of phosphate ions on fired granitic waste immobilized with *Aspergillus niger*

The correlation coefficient R² for the Freundlich isotherm. As shown in table (4) R² moves within narrow range (0.957-0.947) in raw granitic waste and fired granitic waste. It can be also, revealed that no detectable difference between the values of R² in the case of addition of *Aspergillus niger* to the granitic wastes (0.945-0.937).

As observed, experimental data were better fitted to Langmuir equation than to Freundlich equation, and therefore it is more suitable for the analysis of kinetics.

TABLE 4

Freundlich constants calculated from Freundlich isotherm

	R ²	k	n
Raw granitic waste	0.957	0.01	0.51
Fired granitic waste	0.947	0.014	0.56
Raw granitic waste immobilized with <i>Aspergillus niger</i>	0.945	0.01	0.51
Fired granitic waste immobilized with <i>Aspergillus niger</i>	0.937	0.014	0.56

3.1.5. Biosorption studies

The phosphate removal mechanism could be explained by adsorption of the phosphate into the hyphae of the *Aspergillus niger*. So, the biodegradation can occur through the extracellular enzymes produced by *Aspergillus niger* strain. The biosorption study deals with the factors that may affect the biosorption process, such as pH value, adsorbent dose, Effect of initial phosphate concentration, contact time, biomass dosage, isothermal studies and biodegradability studies. There is an increase in the correlation coefficient (R²) for the Langmuir isotherm in the case of addition of *Aspergillus niger* to the raw granitic waste and fired granitic waste which indicates that relative increase in the adsorption efficiency of phosphate ions from wastewater.

3.2. Discussion

Dependence on all of the previous obtained data and calculation that carried out in the recent study it is noticed that the presence of two main mechanisms controlling the adsorption process of phosphate ions by studied granitic wastes respectively called chemical mechanism and mycological respectively. The first one (chemical mechanism) depends on composition of the used granitic waste as its adsorption for phosphate ions from wastewater explained by its possessing the Si-O₂ group (active group) for the adsorption of phosphate group as detected by FTIR. The most stable adsorption geometry involves hydrogen bonding between two Si-OH groups and the O atom of the P=O group [33].

The second one as mentioned before mycological mechanism based on the ability of hyphae of *A. niger* to adsorb the phosphate from wastewater then the biodegradation can occur through the extracellular enzymes produced by *A. niger* strain

agreed with [34] *Aspergillus niger* was used for the treatment of wastewater effluent for their capacity to reduce the effluent parameters especially phosphates.

Finally, the connection between the two main previous mechanisms explained the reason for selecting and expecting the utilization of the used granitic waste as adsorbent for phosphate ions from wastewater.

4. Conclusions

- Generally, the chemical and mineralogical composition of the studied granitic waste indicated that it most likely to be originated from Alkali-Feldspar granite.
- Two main studied mechanisms (chemical and mycological) play important role in phosphate ion adsorption by both of raw and fired granitic wastes.
- The obtained preferable chemical parameters were pH 9 solution, 150 minutes for contact time, 2.5 gm of adsorbent dose and optimum concentration of phosphate adsorption around 25 to 30 mg/l at an ambient temperature 25± 2°C.
- The Langmuir isotherm better fitted the experimental data since the correlation coefficient for the Langmuir isotherm was higher than that of the Freundlich isotherm.
- The addition of *Aspergillus niger* to granitic waste relatively increase the removal efficiency as obtained in the current study.
- The phosphate removal % approximately similar in using both of raw and fired granitic wastes under the studied optimum chemical parameters.
- Generally the use of granitic waste as a new coagulant, eco-friendly, cheap and sustainable materials for phosphate removals from wastewater is an ecologically safe and economically reasonable.

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